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The Effect of Heat Treatment on the Thermal Expansion of Pyrolytic Graphite

AUGUST 1966

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Prepared for BALLISTIC SYSTEMS AND SPACE SYSTEMS DIVISIONS
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
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THE EFFECT OF HEAT TREATMENT ON THE THERMAL EXPANSION OF PYROLYTIC GRAPHITE

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FOREWORD

This report is published by the Aerospace Corporation, El Segundo, California, under Air Force Contract No. AF 04(695)-669.

This report, which documents research carried out from February 1965 to April 1965, was submitted on 16 September 1966 to Captain William D. Bryden, Jr., SSTRT, for review and approval.

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Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

William D. Bryden Jr.

William D. Bryden Jr., Capt USAF
Space Systems Division
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ABSTRACT

Thermal expansion was studied by x-ray techniques for three graphites: a commercially available pyrolytic graphite, PG: the same PG annealed at 3410°C for 1 hr; and AGKSP, a spectrographic grade graphite. The coefficients of thermal expansion along the C-axis α_c for the three materials are respectively: 26.5×10^{-6} (20-2400°C); 27.9×10^{-6} (20-3000°C); and 30.1×10^{-6} (20-2700°C). The value of α_c is found to increase with a decrease in the fraction of disordered layers (p) in the graphite. Discussion of this effect is extended to include the results of other studies.

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I. INTRODUCTION

The growing demands on graphite as an aerospace material make it necessary to know the thermal expansion of selected graphites to increasingly higher temperatures. The determination of thermal expansion for pyrolytic graphite (PG) is complicated, however, by irreversible changes in the structure resulting from heat treatment at temperatures above its deposition temperature. Guentert and Cvikevich include among these changes: increased layer order, increased particle size, reduction in C-direction microstrain, and increased orientation (Ref. 1). The effect of heat treatment on the room temperature C_0-lattice parameter has been investigated by Kotlensky and Martens (Ref. 2), Bragg and Packer (Ref. 3) and Richardson and Zehms (Ref. 4). The resultant effect on the gross thermal expansion as the result of such treatment has beem demonstrated by Pappis and Blum (Ref. 5).

Lowell (Ref. 6) has shown that the crystal lattice thermal expansion is a function of the crystallinity of the graphite. He has suggested two possible reasons for the differences he observed in the thermal expansion of several graphites: (1) pinning of a given crystallite by neighboring crystallites in the untreated graphite grains, thereby reducing the effective thermal expansion, and (2) the presence of carbon atoms which form interlayer cross links, thereby increasing the room-temperature C_0-spacing and reducing thermal expansion along the C-axis. Steward, et al. (Refs. 7 and 8) determined the coefficient of thermal expansion α for two graphites from room temperature to 728°C. They found the coefficient of thermal expansion α to be largely independent of both the interplanar spacing d and fraction of disoriented planes p.

The purpose of this study is to extend the C-axis thermal-expansion data for annealed PG to temperatures up to 3000°C and to ascertain the effect of annealing on the thermal expansion.

II. EXPERIMENTAL

A. MATERIALS

The material used as a control for this experiment was AGKSP graphite, a commercially available manufactured graphite.[1] Pyrolytic graphite specimens were prepared from a 3/4-in. block of continuously nucleated material[2] which was deposited at 2150°C. The heat-treated PG specimens were further annealed at 3410°C for 1 hr in argon. The specimen configuration is shown in Fig. 1.

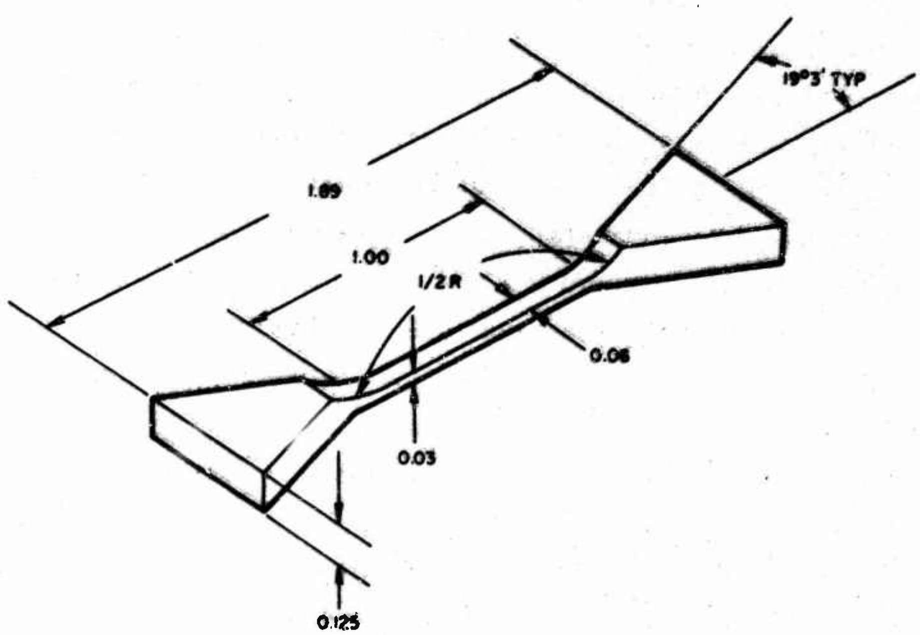

Fig. 1. Configuration of Specimen Used in X-Ray Diffractometer Furnace

[1] National Carbon Company

[2] High Temperature Materials, Division of National Carbon Company

The high degree of anisotropy of the PG required that it be machined so that the basal planes of the graphite were parallel to the major surface of the specimen to permit easy measurement of the 0002 reflection. The orientation of the AGKSP was random with respect to the specimen.

B. PROCEDURE

The x-ray diffractometer furnace used in this study is shown in Fig. 2. Its operation has been described in detail in Ref. 9. Temperature measurements were made with a Micro-Optical Pyrometer. An emissivity of 0.85 (Ref. 10) was used for the AGKSP and 0.95 (Ref. 11) was used for the surface parallel to the C-axis of the PG.

The room temperature lattice parameters of the specimens were obtained using the standard G. E. XRD-5 flat sample diffraction assembly. The furnace was then placed on the x-ray spectrogoniometer and a specimen inserted and aligned on an appropriate x-ray reflection. After purging the furnace with helium, the specimen was heated to 800°C and a diffractograph made of the relevant reflection(s). This procedure was repeated at each temperature and finally at room temperature. The final room temperature pattern for the annealed PG was used to determine the change in observed lattice dimensions during the experiment due to possible sample warpage, furnace alignment, and permanent lattice changes. The maximum change observed from initial to final room temperature measurements was 0.12 percent.

After each run above 2000°C the specimen was cooled to room temperature, and the surface observed with the pyrometer was cleaned to remove a porous recondensed graphite deposit (Ref. 12).

The C_0-values were calculated from the 0002 reflections. Absorption corrections were made using natural graphite crystals as a standard.

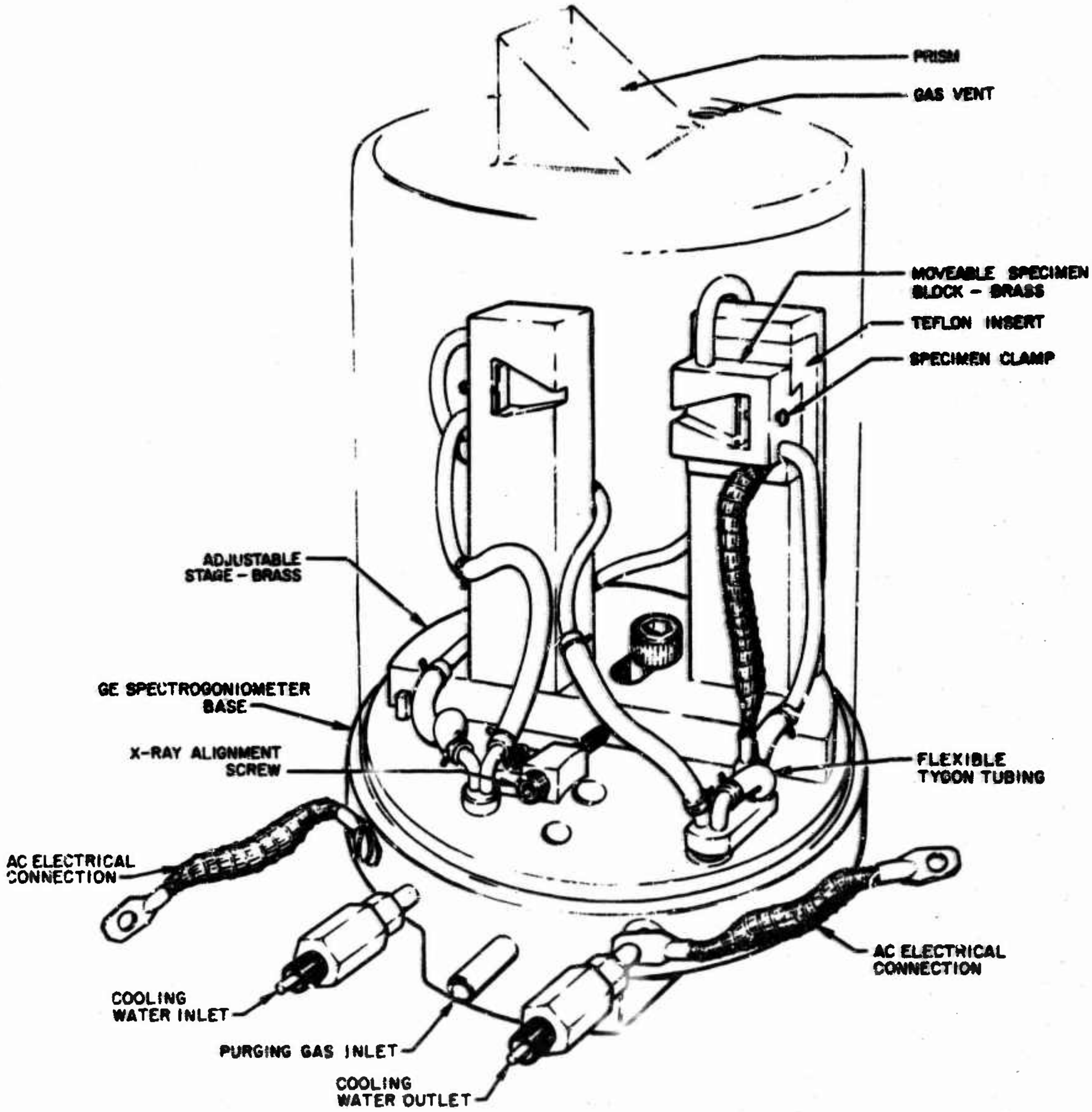

Fig. 2. X-Ray Diffractometer Furnace for G. E. XRD-5 Goniometer (Spectrometer-style base is not shown.)

III. RESULTS AND DISCUSSION

The AGKSP graphite used as a control material had a fraction of disoriented planes $p = 0.34$. The coeffient of thermal expansion for AGKSP in the C_0-direction as determined in this study is $\alpha_c = 30.1 \times 10^{-6}$; Yang (Ref. 13) obtained a value of 31.9×10^{-6} for the same grade of graphite with $p = 0$. The agreement is reasonable if, as discussed below, α is dependent on p.

The C_0-spacing and percent expansion of the AGKSP as a function of temperature are shown in Fig. 3. A slight departure from linearity may be noted for the thermal expansion.

The coefficient of thermal expansion of the "as received" pyrolytic graphite ($p = 0.83$) is $\alpha_c = 26.5 \times 10^{-6}$ from 20 to 2100°C. Thermal expansion above 2400°C was not reported for this material because the lattice dimensions are also influenced by the irreversible changes in the structure mentioned earlier (Ref. 4). The C_0-lattice dimensions and the percent expansion as a function of temperature are shown in Fig. 4 for the "as received" PG.

The coefficient of thermal expansion in the C_0-direction for the annealed PG is $\alpha_c = 27.9 \times 10^{-6}$ from 20 to 3000°C. The C_0-lattice dimension and percent expansion as a function of temperature for the annealed PG is shown in Fig. 5. The fraction of disoriented layers in this material was $p = 0.39$.

The effect of annealing on the PG was to reduce the room-temperature C_0 from 6.834 Å to 6.744 Å. According to the generally accepted views of Bacon (Ref. 15) and Franklin (Ref. 16) this signifies a decrease in the fraction of disoriented layers p as a result of annealing. The thermal expansion in the C_0-direction was also measurably increased as a result of this treatment. Thus it would seem that the coefficient of thermal expansion is dependent on p. This observation may be extended to include the following data: (1) AGKSP graphite used in this study, (2) Lowell (Ref. 6), (3) Yang (Ref. 13), and (4) Steward, et al. (Ref. 8). The α and p for the various graphite in these studies are listed in Table I, where we see that in general the thermal

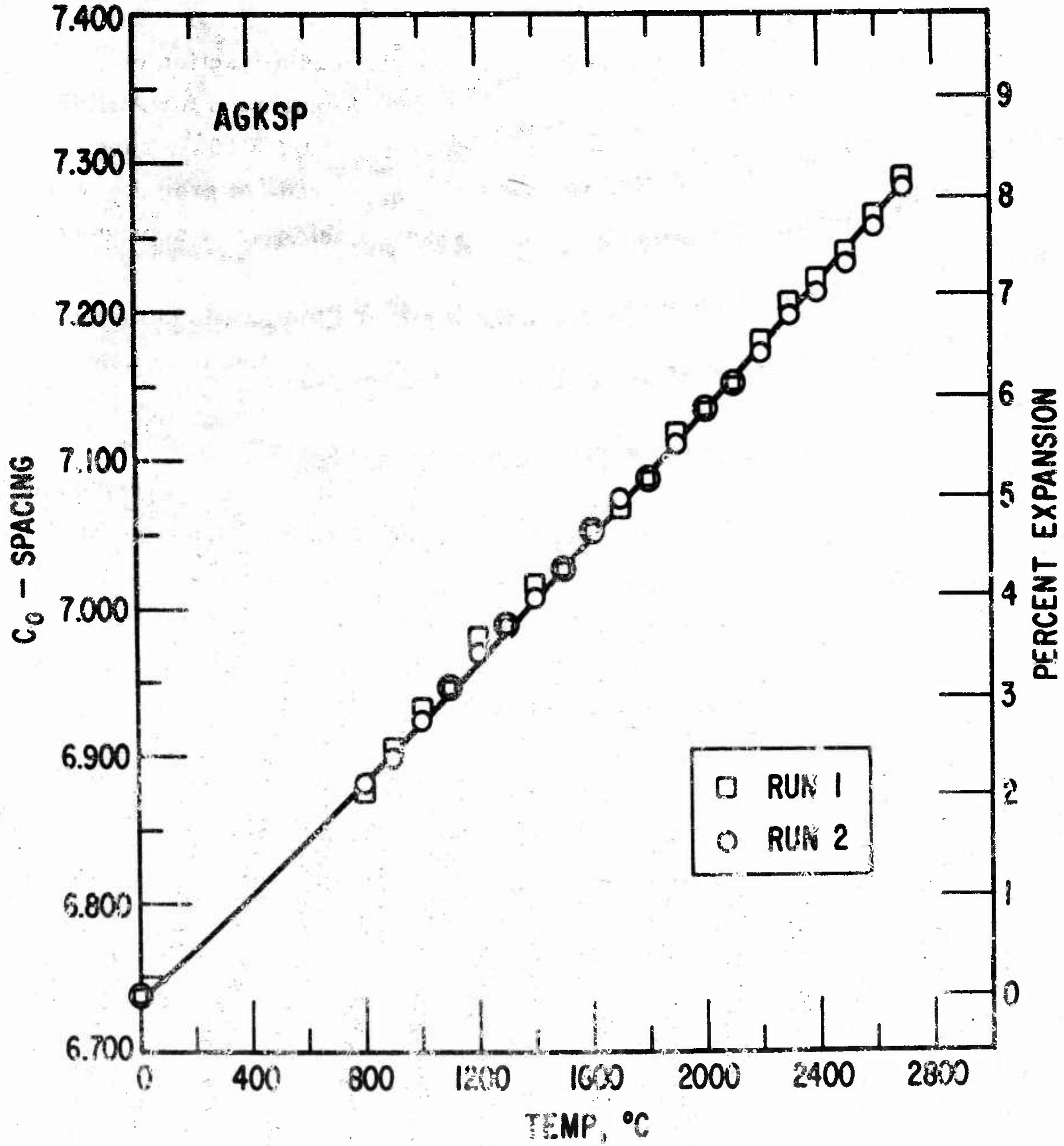

Fig. 3. C_0-Lattice Dimensions and Percent Thermal Expansion for AGKSP Graphite as a Function of Temperature

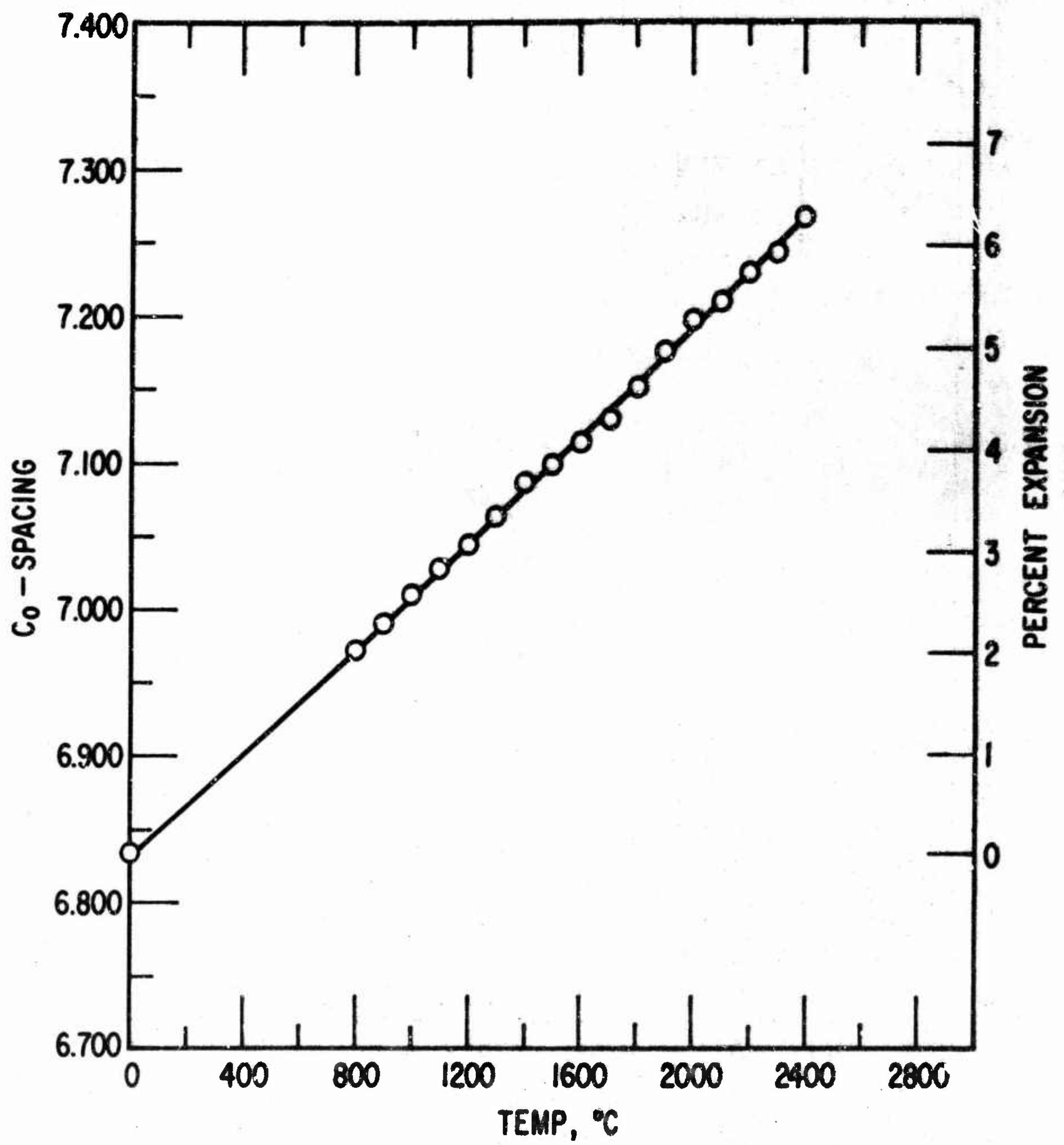

Fig. 4. C_0-Lattice Dimensions and Percent Thermal Expansion for Unannealed Pyrolytic Graphite as a Function of Temperature

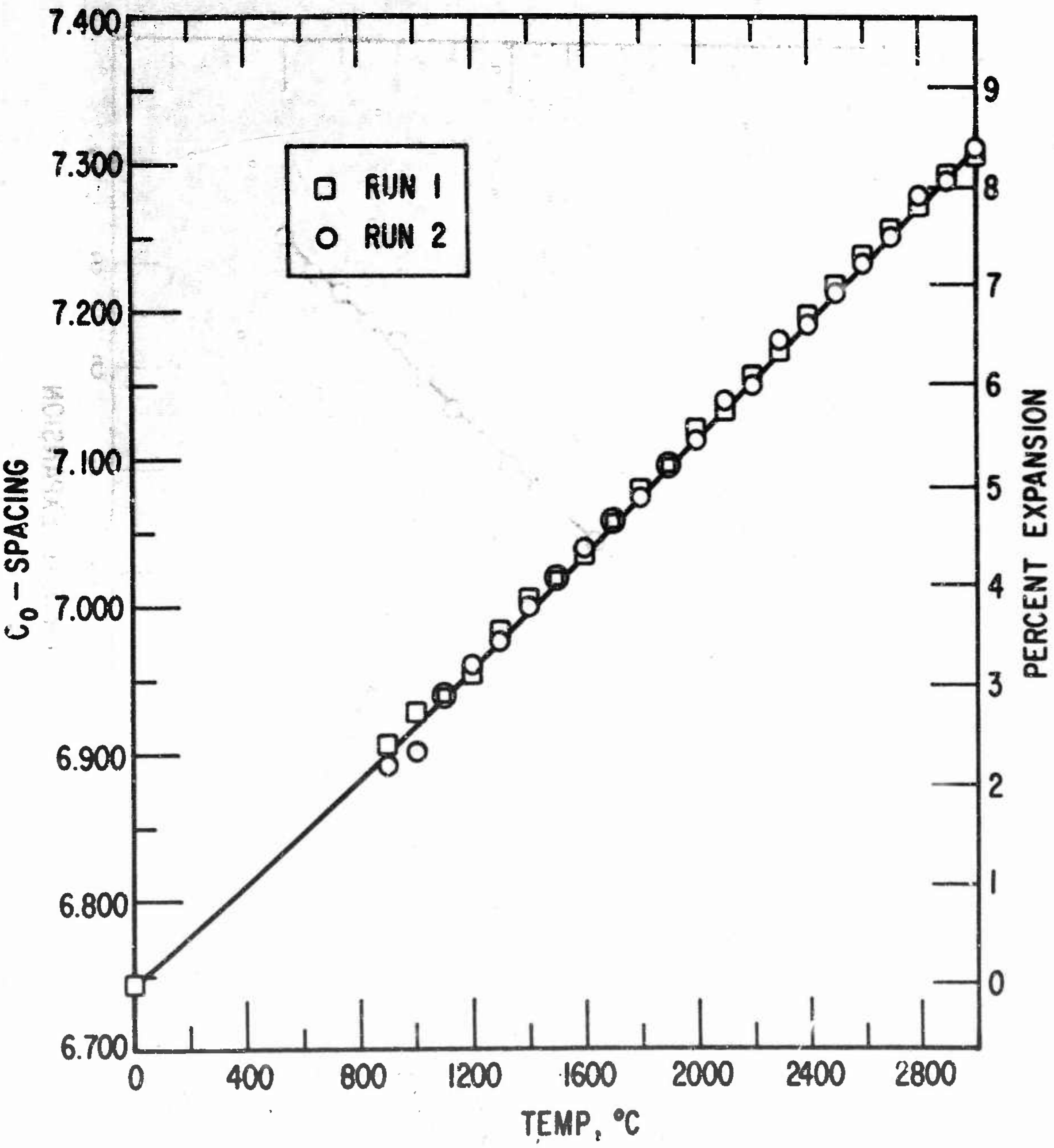

Fig. 5. C_0-Lattice Dimension and Percent Thermal Expansion as a Function of Temperature for Pyrolytic Graphite Treated at 3140°C for 1/2 hr

Table I. Coefficient of Thermal Expansion (TE) and Fraction of Disoriented Layers for Several Graphites

Fraction of Disoriented Layers (p)	Temperature Range, °C	Coefficient of Thermal Expansion $\times 10^{-6}(\alpha)$	Reference
0	20-2600	31.9	Yang
0.05	20-2527	32.8	Lowell
0.13	-196-2600	31.6	Steward, Cook & Kellett
0.24	20-2527	29.4	Lowell
0.34	20-2700	30.1	Present
0.39	20-3000	27.9	Present
0.54	20-2400	29.2	Yang
0.72	20-2527	27.9	Lowell
0.83	20-2100	26.5	Present

expansion decreases as p increases. It is not clear at this time how thermal expansion is thus influenced, but various mechanisms have been proposed to explain the phenomenon (Refs. 3 and 6).

IV. CONCLUSION

The results of this study are summarized as follows:

1. The coefficient of linear thermal expansion along the C-axis for a 2150°C-deposited PG is $\alpha_c = 26.5 \times 10^{-6}\,{}^\circ C^{-1}$ (20-2100°C). Measurements above 2400°C were not reported because of irreversible contractions resulting from structural changes which start to occur at this temperature in addition to the thermal expansion.

2. Specimens of the 2150°C-deposited pyrolytic graphite were heat-treated at 3410°C for 1 hr in argon to remove the effects of the irreversible contractions resulting from the changes mentioned above. The coefficient of linear expansion for this material along the C-axis is $\alpha_c = 27.9 \times 10^{-6}\,{}^\circ C^{-1}$ (20-3000°C).

3. The coefficient of linear expansion along the C-axis for AGKSP spectrographic graphite is $\alpha_c = 30.1 \times 10^{-6}\,{}^\circ C^{-1}$ (20-2700°C).

4. Heat treatment of the pyrolytic graphite resulted in an increase in α_c and a reduction in p (indicated by a decrease in the C_0-spacing). These results have been compared with those of other lower temperature studies; all results demonstrate a general dependence of α on p.

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